# RECENT DEVELOPMENTS IN COAL LIQUEFACTION AND COPROCESSING AT FETC (OST)

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## Introduction

Recent coprocessing research at FETC has shown:

1. Coal facilitates the demetalation of heavy oils and/or resids even at low coal concentrations (2-5 wt%). In addition, other solid carbon surfaces can be used in place of coal for the demetalation.[1]

2. Slurry catalysts are effective for coal liquefaction and coprocessing. These include a high surface area $MoS_2$ (surface area of 260 $m^2/g$) and impregnated FeOOH.[2]

3. Pressure can be reduced in coal liquefaction through a combination of solvent quality and catalyst concentration.[3]

4. The addition of coal suppresses 2-ring aromatic hydrogenation.[4]

5. Catalyst activity can be correlated with the physical properties of dispersed catalysts (crystallite size, surface area, and initial contact with coal).[5]

The research conducted in FY97 was directed toward the following areas:

1. A comparison of donor solvent to non-donor solvent systems.

2. Testing of a series of coals to evaluate the impact on catalytic coal liquefaction and coal/oil coprocessing.

3. A comparison of dispersed with supported catalysts.

4. Exploratory research to evaluate the effect of pressure reduction in coprocessing.

The overall objectives of the work were to evaluate coal liquefaction catalysts for coal/oil coprocessing and heavy oil upgrading and demonstrate the potential for pressure reduction.

## Experimental:

**Materials** - The reactants used include Hondo resid (vacuum tower bottoms) and fluid catalytic cracking (FCC) decant oil. The Hondo resid was an $850^{o}F^{+}$ boiling material from a vacuum distillation tower. The FCC decant oil was a distillate product from an FCC unit and contained 36% $850^{o}F^{+}$ boiling material. Illinois No. 6 and Blind Canyon bituminous coals were used for the majority of the tests. A series of microautoclave tests was conducted using several different coals identified in the discussion section. Several unsupported catalysts were investigated including aqueous ammonium heptamolybdate (AHM), preformed $MoS_2$ (surface area of 260 $m^2/g$ generated from aqueous AHM), Moly-Van-A, Moly-Van-L, sulfated iron oxide and FeOOH impregnated on coal[2]. The supported catalyst was a commercial NiMo/$\gamma$-$Al_2O_3$ catalysts(Akzo AO-60).

**Reactors** - Three types of reactors were used in this study; microautoclave, 1-L semi-batch, and 1-L continuous. The microautoclave reactor is a 43 mL tubular reactor. The 1-L semi-batch reactor employs a flowing gas, batch slurry system (typically 400 g charge). The 1-L continuous reactor is a flowing gas/flowing slurry (typically 200- 400 g/h of slurry). These reactor systems and the product work-up procedures used in these systems have been described previously[2].

**Discussion:**

Effect of hydrogen delivery:

Recently FETC personnel have been studying 2-ring aromatic donor and non-donor solvent systems with and without catalysts. Rothenberger et al. reported these results and concluded that conversion could be predicted from the amount of hydrogen delivered from either the gas phase (facilitated by the presence of a catalyst) or by donation from the solvent. Figure 1 shows the relationship between conversion (both to THF and heptane solubles) and hydrogen delivered (from either the gas phase or donor solvent) observed in this study. Included in these data are tests with and without catalysts, donor and non-donor solvents, and times from 2 to 30 minutes. The figure indicates that the conversion is related to the hydrogen delivered to coal regardless of the delivery system (gas phase hydrogenation or solvent donated hydrogen).

Effect of coal type:

The effect of coal type on catalytic coal liquefaction and coprocessing was studied in a series of microautoclave tests. The coals and conversion and hydrogen consumptions observed in these tests are shown in Table 1. Figures 2 through 4 show the effect of carbon, ash, and sulfur content on conversion. It appears that carbon and sulfur content are more predictive of conversion than ash content.

Effect of catalyst type:

A series of tests was conducted to investigate the effect of catalyst type. The catalysts studied in these tests were Moly-Van-A, Moly-Van-L (with and without added carbon black), and AO-60. The results of these tests for coal liquefaction and heavy oil upgrading are shown in Figures 5 and 6. These results indicate that the two dispersed catalysts (Moly-Van-A and Moly-Van-L) are at least as active as the AO-60 for coal liquefaction. Similar results were observed with Hondo hydrogenation. However, the hydrogen consumed with Moly-Van-A was much higher than the hydrogen consumed with any of the other catalysts tested.

Effect of pressure reduction:

The effect of pressure reduction was studied in a series of continuous tests. The feeds consisted of either FCC decant oil or Hondo resid (90 wt%) and Illinois No. 6 coal (10 wt%). The catalyst used was an aqueous ammonium heptamolybdate (AHM). The effect of pressure reduction and catalyst concentration was investigated in this series. The results are shown in Table 2. The results indicate (for the FCC decant oil case) that increasing catalyst concentration increases 850$^{o}$F+ conversion at lower pressures (as low as 500 psig). Also, at 500 ppm Mo, there was no effect of increasing pressure from 1500 to 2500 psig on 850$^{o}$F+ conversion. With Hondo resid, increasing the catalyst concentration from 100 to 500 ppm at 1500 psig increased 850$^{o}$F+ conversion. Recent tests (the conversion results are not available) indicate that 30 wt% coal in Hondo resid could be operated at pressures as low as 1000 psig. The test encompassed 200 hours of continuous operation at these conditions.

## Conclusions:

The hydrogen delivery study indicated that coal conversion could be predicted based on hydrogen delivered to the coal (summing the contributions from the gas phase and donor solvent). Coal type affects first stage coal liquefaction and coprocessing. In addition, it appears that conversion correlates best with carbon and sulfur content.

Pressure reduction can be compensated by increases in catalyst concentration in coal/oil coprocessing. In addition, stable continuous operations are achievable at lower pressures (as low as 500 psig with 10 wt% coal and 1000 psig with 30 wt% coal).

## Disclaimer:

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